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(54) Title: ORGANOPHOSPHOROUS COMPOSITIONS

(57) Abstract: The efficacy of insecticidal compositions (especially organophosphate insecticides) is enhanced through the blending of the insecticide with fatty acid containing crop oil concentrate.

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## ORGANOPHOSPHOROUS COMPOSITIONS

Pesticides, especially organophosphate insecticides, have come  
5 under increased scrutiny. Specifically, the Food Quality  
Protection Act of 1996 (FQPA) mandates that the EPA reassess all  
pesticide tolerances and exemptions from tolerances by 2006.  
There is a need for insecticidal compositions which are more ef-  
ficacious or which retain their efficacy at lower doses.

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As discussed in U.S. 5,326,560 to Henderson, the art has attempt-  
ed to manage the problem of insecticide toxicity in the environ-  
ment through careful selection and application of herbicides and  
pesticides. As described therein, ideal application of insectici-  
15 des to crops might involve applying minimal quantities of insecti-  
cides which maintain effectiveness over a longer period of  
time. Many insecticides currently available, such as pyrethrum,  
the pyrethroids, organophosphates, and biologicals, rapidly de-  
grade after exposure to ultraviolet radiation and/or through hy-  
20 drolysis and oxidation. Unfortunately, these active ingredients  
may degrade well before they have accomplished their purpose. To  
address these problems, Henderson discloses an insecticide  
carrier that is a mixture of petrolatum (preferably white petro-  
latum), diatomaceous earth, and preferably a diluent, such as  
25 "crop oil." Henderson reports that low rates of the insecticidal  
toxicant (a bacterial insecticide) are more effective when used  
in combination with the proper carrier/adjuvant. It should be  
considered, however, that increased persistence of pesticidal re-  
sidues may not be advantageous in all cases because, for example,  
30 they might be ingested by the consumer of the produce.

JP 58-172304 discloses an ant control agent comprising organo-  
phosphorus insecticides plus anionic and nonionic surfactants  
which is applied to wood surfaces. The anionic surfactant is pre-  
35 ferably dodecylbenzene calcium sulfonate. The non-ionic  
surfactant is polyoxyethylene alkylphenol-ether. The ant control  
agent reportedly permeates the wood and adheres to the wood  
surface better than the prior art materials.

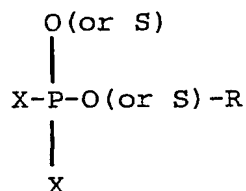
40 JP 9-268108A discloses a low dose organophosphorus compound  
(e.g., acephate), non-ionic and/or anionic surfactants and a so-  
lid carrier having a specified degree of whiteness. The working  
examples in JP 9-268108A teach the use of non-ionic or anionic  
surfactants. Both types of surfactants in one formulation are not  
45 taught.

At col. 8, lines 45-47, U.S. 5,108,488 teaches that when the herbicidal composition described therein is to be used as a pre-emergent treatment for weed control. A fertilizer, an insecticide, a fungicide, or another herbicide may be included in the formulation.

U.S. Patent No. 5,399,542 is also directed to herbicidal compositions which may further contain an adjuvant, including a mixture of petroleum hydrocarbons, alkyl esters and acids, anionic surfactants and inert materials, e.g., DASH® adjuvant available from BASF Corporation.

U.S. Patents No. 4,966,728 and 5,084,087 describe adjuvants that are useful for herbicide formulations.

Organophosphorus compounds, such as organophosphates, are anticholinesterase chemicals which damage or destroy cholinesterase, the enzyme required for nerve function in the living body. Various alkoxy groups (X) are often attached to the phosphorus as follows:



The term "necessary effective dose", as used herein, means the dose at which a desired pesticidal activity is achieved.

The term "effective", as used herein, means the typical amount, dosage or concentration or percentage of an active ingredient necessary to achieve a desired result.

The term "carrier", as used herein, means an inert material added to a technical toxicant to facilitate later dilution to field strength.

The term "diluent", as used herein, means a material, liquid or solid, serving to dilute the technical toxicant to field strength for adequate plant coverage, maximum effectiveness and economy.

The term "HLB", as used herein, means hydrophilic/lipophilic balance. For example, emulsifiers typically involve a molecule that combines hydrophilic and lipophilic groups. The hydrophilic/lipophilic balance (HLB) is a major factor in determining the emulsification characteristics of a non-ionic surfactant. Surfactants with lower HLB values are more lipophilic, while surfactants with

higher HLB values are more hydrophilic. These HLB values assist formulators by reducing the number of surfactants to be evaluated for a given application. In general, surfactant function falls within specific HLB ranges, noted below:

5	<u>HLB</u>	<u>Surfactant Function</u>
	4-6	Water/oil emulsifier
	7-9	Wetting agent
	8-18	Oil/water emulsifier
10	13-15	Detergent
	10-18	Solubilizer

In the present application, all percentages are weight percent unless otherwise indicated.

15

It is an object of the present invention to provide more efficacious organophosphorus insecticidal compositions containing an organophosphorus insecticide, an adjuvant and, optionally, a diluent.

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Another object of the present invention is to provide organophosphorus insecticidal compositions that demonstrate substantially equivalent efficacy at reduced application rates.

25 In accordance with these objects, it has been discovered that blending an organophosphorus insecticidal composition with a certain class of adjuvant enables the use of lower levels of said insecticide while maintaining the active ingredient's effectiveness. Also, such blending improves the efficacy of certain organophosphorus insecticides at equivalent application rates.

30 Thus, in one embodiment the present invention is an insecticidal composition composed of from 0.015% to 3.6% of one or more organophosphate insecticidal compounds; from 0.5% to 99.5% of an adjuvant composition comprising, based on the weight of the adjuvant:

- (a) from 20 to 90 weight percent of a C<sub>1</sub>-C<sub>6</sub>-alkanol ester of a fatty acid containing from 4-22 carbon atoms;
- 40 (b) from 4 to 40 weight percent of an anionic surfactant selected from the group consisting of partial sulfate and phosphate esters and carboxylates of monohydroxyfunctional polyoxyalkylene ethers;
- (c) from 2 to 20 weight percent of a long chain carboxylic acid
- 45 containing from about 10 to about 20 carbon atoms; and
- (d) optionally, a hydrocarbon;
- and diluent.

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In another embodiment, the insecticidal composition is composed of 0.5% - 99.5% of an adjuvant composition comprising, based on the weight of the adjuvant:

- 5 (a) from 30 to 80 percent of a C<sub>1</sub>-C<sub>6</sub>-alkanol ester of a fatty acid containing from 10 to 20 carbon atoms;
  - (b) from 4 to 20 percent of an anionic surfactant selected from the group consisting of the partial sulfate and phosphate esters and carboxylates of monohydroxyl-functional polyoxy-
  - 10 alkylene ethers having an average molecular weight of from 600 to 1200 Daltons; and
  - (c) from 4 to 6 percent of a long chain carboxylic acid having from 10 to about 20 carbon atoms;
- 15 0.015% to 3.6% of one or more organophosphate insecticidal compound;  
and diluent.

Another embodiment of the present invention is an insecticidal  
20 composition composed of 0.5% - 99.5% of an adjuvant composition comprising, based on the weight of the adjuvant:

- (a) from 2 to 30 percent of an anionic surfactant selected from the group consisting of the partial sulfate and phosphate
- 25 esters and carboxylates of monohydroxyl-functional polyoxy-alkylene ethers and their alkali metal, alkaline earth metal and ammonium salts;
- (b) one of the following fatty acid components:
  - (i) from 1 to 20 percent of a fatty acid having from 10 to 22
  - 30 carbon atoms; and
  - (ii) from 10 to 96 percent of a C<sub>1</sub>-C<sub>6</sub>-alkanol ester of a fatty acid having from 10 to 22 carbon atoms; and
- (c) a hydrocarbon component with is
  - (i) from 90 to 10 percent when the fatty acid component is
  - 35 (b) (i); and
  - (ii) up to about 70 percent when the fatty acid component is (b) (ii);

0.015% - 3.6% of one or more organophosphate insecticidal  
40 compounds; and diluent.

Another aspect of the present invention is a method for controlling insect populations in crops. The method involves applying to said crop an effective amount of one of the insecti-  
45 cidal compositions described above. It is method is especially

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efficacious when used to control insect populations or the lepidopteran order.

The preferred organophosphorus compounds useful in the practice of the present invention are represented by the following structures:

Phosphate (e.g. dictrotophos):



15 Phosphorothioate (e.g. parathion):



25 Phosphorothioate (e.g. cyanothorate):



Phosphorothioate (e.g. phorate):



40 Phosphonate (e.g. trichlorfon):



6

Phosphoramidate (e.g. crufomate):



- Specific organophosphorus compounds useful in the practice of the present invention include, but are not limited to,
- O,S-dimethyl acetylphosphoramidothioate, CAS Number 30560-19-1 (Acephate);
- S-[2-(formylmethylamino)-2-oxoethyl]O,O-dimethyl phosphorodithioate, CAS Number 2540-82-1 (Formothion);
- 15 S-6-chloro-2,3-dihydro-2-oxo-oxazolo[4,5-b]pyridin-3-yl-methyl]O,O-dimethyl phosphorothioate, CAS Number 35575-96-3 (Azamethiphos);
- O,O-diethyl S-[4-oxo-1,2,3-benzotriazin-3(4H)-yl)-methyl]phosphorodithioate, CAS Number 2642-71-9 (Azinphos-ethyl);
- 20 O,O-dimethyl S-[4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl]-phosphorodithioate (CAS 9CI), CAS Number 86-50-0 (Azinphos-methyl);
- 2-chloro-1-(2,4-dichlorophenyl)vinyl diethylphosphate, CAS Number 470-90-6 (Chlorfenvinphos);
- O,O-diethyl-O-3,5,6-trichloro-2-pyridyl phosphorothioate, CAS Number 2921-88-2 (Chlorpyrifos);
- O-4-cyanophenyl O,O-dimethyl phosphorothioate, CAS Number 2636-26-2 (Cyanophos);
- S-[(4-chlorophenyl)thio]methyl O,O-diethyl phosphorothioate (IUPAC), CAS Number 786-19-6 (Danifos);
- 30 O,O-diethyl O-[4-methylsulfinyl]phenyl) phosphorothioate, CAS Number 115-90-2, (Fensulfothion);
- S,S,S-tributyl phosphorotrithioate, CAS Number 78-48-8 (Tribufos);
- O,O-diethyl O-[6-methyl-2(1-methylethyl)-4-pyrimidinyl] phosphorothioate (CAS 9CI);
- 35 O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate (CAS 8CI), CAS Number 333-41-5 (Active ingredient of Diazinon);
- (E)-2-dimethylcarbamoyl-1-methylvinyl dimethyl phosphate, CAS Number 141-66-2 (Dicrotophos);
- O,O-dimethyl S-methylcarbamoylmethyl phosphorodithioate, CAS Number 60-51-5 (Dimethoate); S,S'-(1,4-dioxane-2,3-diyl) O,O,O',O'-tetraethyl bis (phosphorodithioate), CAS Number 78-34-2 (Dioxathion);
- 45 O,O-diethyl S-[2-(ethylthio)ethyl] phosphorodithioate, CAS Number 298-04-4 (Disulfoton);

- S-5-methoxy-4-oxo-4H-pyran-2-ylmethyl O,O-dimethyl phosphorothioate, CAS Number 2778-04-3 (Endothion);  
O,O,O',O'-tetraethyl S,S'-methylene bis(phosphorodithioate), CAS Number 563-12-2 (Ethion);
- 5 O,O-dimethyl O-4-nitro-m-tolyl phosphorothioate, CAS Number 122-14-5 (Fenitrothion);  
O-ethyl S,S-dipropyl phosphorodithioate, CAS Number 13194-48-4 (Ethoprop);  
O,O-diethyl O-(1,2,2,2-tetrachloroethyl) phosphorothioate, CAS Number 54593-83-8 (Chlorethoxyfos);
- 10 S-benzyl O,O-di-isopropyl phosphorothioate, CAS Number 26087-47-8 (Iprobenfos);  
O-5-chloro-1-isopropyl-1H-1,2,4-triazol-3-yl O,O-diethyl phosphorothioate, CAS Number 42509-80-8 (Isazofos);
- 15 1-methylethyl 2-[[ethoxy[(1-methylethyl)amino]phosphinothioyl]osyl]benzoate, CAS Number 25311-71-1 (Isofenphos);  
O,O-Diethyl O-(5-phenyl-3-isoxazolyl) phosphorothioate, CAS Number 18854-01-8 (Isoxathion);  
O,O-dimethyl S-2-(1-methylcarbamoylethylthio)-ethyl phosphorothioate, CAS Number 2275-23-2 (Vamidothion);
- 20 S-[2-(ethylsulfinyl)-1-methylethyl] O,O-dimethyl phosphorothioate, CAS Number 2674-91-1, (Active Ingredient of Metasystox-S) S-2,3-dihydro-5-methoxy-2-oxo-1,3,4-thiadiazol-3-ylmethyl O,O-dimethyl phosphorodithioate, CAS Number 950-37-8 (Methidathion);
- 25 O,O-dimethyl O-(4-nitrophenyl) phosphorothioate, CAS Number 298-00-0 (Methyl Parathion);  
Alpha isomer of 2-carbomethoxy-1-methylvinyl dimethyl phosphate (typical 63%);  
Beta isomer of 2-carbomethoxy-1-methylvinyl dimethyl phosphate (typical 25%), CAS Number 7786-34-7 (Mevinphos);
- 30 S-morpholinocarbonylmethyl phosphorodithioate, CAS Number 144-41-2, (Morphothion);  
1,2-dibromo-2,2-dichloroethyl dimethyl phosphate, CAS Number 300-76-5 (Naled);
- 35 Ethyl 3-methyl-4-(methylthio)phenyl (1-methylethyl)-phosphoramidate (CAS), CAS Number 22224-92-6 (Fenamiphos);  
S-[N-(2-chlorophenyl) butyramidomethyl]O,O-dimethyl phosphordithioate, CAS Number 83733-82-8, (Fosmethilan);  
O-(1,6-dihydro-6-oxo-1-phenylpyridazin-3-yl) O,O-diethyl phosphorothioate, CAS Number 119-12-0 (Pyridaphenthion);
- 40 O,O-dimethyl S-[2-(methylamino)-2-oxoethyl] phosphorothioate, CAS Number 1113-02-6; (Omethoate);  
O,O-diethyl O-(4-nitrophenyl) phosphorothioate, CAS Number 56-38-2 (Parathion);
- 45 S-2,5-dichlorophenyl-thiomethyl O,O-diethyl phosphorodithioate, CAS Number 2275-14-1 (Phencapton);



- S-( $\alpha$ -ethoxycarbonylbenzyl) O,O-dimethyl phosphorodithioate, CAS Number 2597-03-7 (Phenthoate);  
O,O-Diethyl S-[(ethylthio)methyl] phosphorodithioate, CAS Number 298-02-2 (Phorate);
- 5 S-[(6chloro-2-oxo-3(2H)-benzoxazolyl) methyl] O,O-diethyl phosphorodithioate (CAS), CAS Number 2310-17-0 (Phosalone);  
S-[1,3-dihydro-1,3-dioxo-2H-isoindol-2-yl)methyl] O,O-dimethyl phosphorothioate (CAS 9CI), CAS Number 732-11-6 (Phosmet);  
O-4-Chloro-3-nitrophenyl O,O-dimethyl phosphorothioate, CAS Num-  
10 ber 2463-84-5 (Phosnichlor);  
2-chloro-2-diethylcarbamoyl-1-methylvinyl dimethyl phosphate, CAS Number 13171-21-6 (Phosphamidon);  
O-(4-bromo-2,5-dichlorophenyl) O-methyl phenylphosphonothioate, CAS Number 21609-90-5, (Leptophos);
- 15  $\alpha$ -[[[(diethoxyphosphinothioyl)oxy]imino] benzeneacetonitrile, CAS Number 14816-18-3 (Phoxim);  
O-(2-diethylamino-6-methylpyrimidin-4-yl) O,O-dimethyl phosphorothioate, CAS Number 29232-93-7 (Pirimiphos-methyl);  
O-2-diethylamino-6-methylpyrimidin-4-yl O,O-diethyl phosphoro-  
20 thioate, Number CAS 23505-41-1 (Pirimiphos-ethyl);  
O-ethyl S-propyl phosphorothioate, CAS Number 41198-08-7 (Pro-fenofos);  
S-(2,3-dihydro-5-isopropoxy-2-oxo-1,3,4-thiadiazol-3-yl)methyl O,O-diethyl phosphorodithioate, CAS Number 20276-83-9 (Prothida-  
25 thion);  
O,O-Diethyl S-(N-isopropylcarbamoylmethyl) phosphorodithioate, CAS Number 2275-18-5 (Prothoate);  
S-2-methylpiperidinocarbonylmethyl O,O-dipropyl phosphorodithioate;
- 30 S-[2-(2-methyl-1-piperidiny)-2-oxoethyl] O,O-dipropyl phosphorodithioate, CAS Number 24151-93-7 (Piperophos);  
O-(2,6-Dichloro-4-methylphenyl) O,O-dimethyl phosphorothioate, CAS Number 57018-04-9 (Tolclofos-methyl); O,O-Dimethyl  
O-(2,4,5-trichlorophenyl) phosphorothioate, CAS Number 299-84-3  
35 (Ronnel);  
O-ethyl S,S-di-sec-butyl phosphorodithioate or O-ethyl S,S-bis(1-methylpropyl) phosphorodithioate), CAS Number 95465-99-9 (Cadusafos);  
5-methoxymethylcarbamolymethyl O,O-dimethyl phosphorodithioate,  
40 CAS Number 919-76-6 (Sophamide);  
Demeton, CAS Number 8065-48-3 (mixture of demeton-O (O,O-diethyl O-2-(ethylthio)ethylphosphorothioate) CAS 298-03-3) and demeton-S (O,O-diethyl S-2-(ethylthio)ethylphosphorothioate) CAS 126-75-0); (Demeton I (thiono isomer)) and (Demeton II (thiolo isomer));
- 45 S-2-ethylsulfinylethyl O,O dimethylphosphorothioate, CAS Number 301-12-2 (Oxydemeton-methyl);

- S-[N-(1-cyano-1-methylethyl) carbamoylmethyl] O,O-diethyl phosphoro-thioate, CAS Number 3734-95-0 (Cyanthoate);  
O-[2-(1,1-Dimethylethyl)-5-pyrimidinyl]O-ethyl O-(1-methylethyl) phosphorothioate, CAS Number 96182-53-5 (Tebupirimfos);  
5 S-[[1,1-Dimethylethyl)thio]methyl] O,O-diethyl phosphorodithioate, CAS Number 13071-79-9 (Terbufos);  
(Z)-2-chloro-1-(2,4,5-trichlorophenyl) vinyl dimethyl phosphate, CAS Number 22248-79-9 (Tetra Chlorvinphos);  
S-[2-(ethylthio)ethyl] O,O-dimethyl phosphoro-dithioate (CAS 8  
10 and 9 CI), CAS Number 640-15-3 (Thiometon);  
O-(2,4-dichlorophenyl) O-ethyl S-propyl phosphodithioate, CAS Number 34643-46-4 (Prothiofos);  
S-2-Chloro-1-phthalimidoethyl O,O-diethyl phosphorodithioate, CAS Number 10311-84-9 (Dialifos);  
15 Dimethyl (2,2,2-trichloro-1-hydroxyethyl) phosphonate, CAS Number 52-68-6 (Trichlorfon).

The preferred organophosphorus insecticides are chlorpyrifos, parathion, ethylmethyl parathion, methyl parathion, dimethoate,  
20 azinphosmethyl, acephate, diazinon, malathion, ethion, and fonofos. The more preferred of these organophosphorus compounds are chlorpyrifos, parathion, ethyl-methyl parathion, methyl parathion, dimethoate, azinphosmethyl, acephate, diazinon and malathion. Especially chlorpyrifos, oxydementon-methyl, dimethoate,  
25 methyl parathion, azinphosmethyl, parathion, ethyl-methyl parathion and certain combinations of these.

Particular preferred are compositions containing only one organophosphorus compound selected from the group methyl parathion,  
30 oxydementon-methyl, dimethoate, acephate, dicrotophos and azinphosmethyl, and optionally a second compound selected from the group of the aforementioned preferred organophosphorus insecticides.

35 The concentration of insecticidal compound in the insecticidal composition of the present invention will depend on the specific insecticide used and the specific adjuvant composition. Generally, the insecticidal compound will be present at from 0.015 % to 3.6 % of the composition as applied to the substrate, e.g.,  
40 the plant. More preferably, the insecticidal compound will be present at from 0.015% to 1.8% of the composition as applied to the substrate.

Adjuvant compositions useful in the practice of the present invention  
45 include those based on methylated seed oils such as described in US Patents No. 4,834,908; 5,102,442 and 5,238,604, which are incorporated herein by reference in their entirety for

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the adjuvants described therein. Representative preferred adjuvants are described in U.S. Patent No. 4,834,908 as a mixture of:

- 5 (a) an anionic surfactant derived from esterification of a polyoxyalkylene nonionic surfactant with a dihydric or trihydric inorganic acid or by carboxylation with an organic acid derivative;
- (b) (i) a long chain carboxylic acid and/or (ii) lower alkanol ester thereof; and
- 10 (c) a hydrocarbon.

The anionic surfactants of (a) are preferably the partial sulfate and phosphate esters of polyoxyalkylene ethers. These partial

15 esters are prepared by methods well known to those skilled in the art, for example, by reacting on of the well known and commercially available monohydric polyoxyalkylene ethers with sulfuric acid or phosphoric acid or their chemical equivalents. The sulfate esters so obtained consist predominantly of the half ester

20 (monoester) while the phosphate esters generally contain both mono- and diesters. Also useful, are the carboxylate surfactants, as are also the simple salts of these surfactants, for example the alkali metal, alkaline earth metal or ammonium salts, particularly the latter. The preferred nonionic, monofunctional ethers

25 used to prepare the esters are available commercially. The preferred ethers have molecular weights of from 400 to 3000 Daltons, more preferably, from 600 to 1200 Daltons. An exemplary anionic surfactant is KLEARFAC® AA-270, a phosphate ester product of BASF Corporation, Mt. Olive, NJ, USA.

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The long chain carboxylic acid component (b) (i) may have a chain length of from 10 to 22 carbon atoms. Preferably, the carboxylic acid component is selected from the group of naturally occurring fatty acids such as stearic acid, linoleic acid, palmitic acid,

35 oleic acid and the like and mixtures thereof. The unsaturated fatty acids are preferred. The long chain carboxylic acid ester component (b) (ii) may be considered as derived from a lower alkanol having from 1 to 4 carbon atoms, such as methyl alcohol, ethyl alcohol, propyl alcohol or butyl alcohol and a long chain

40 carboxylic acid. The methyl and ethyl esters are preferred. Most particularly, the methyl esters are utilized. The long chain carboxylic acid generally contains from 10-22 carbon atoms, preferably from 14-18 carbon atoms. Preferred are those carboxylic acids obtainable from natural sources such as fats and

45 oils, for example, lauric, myristic, stearic, linoleic, linole-

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nic, palmitic and oleic acids. Mixtures of these acids are also useful. Preferred are methyl esters of oleic and palmitic acids.

The hydrocarbon component (c) may be derived principally from  
5 vegetable or petroleum sources. Hydrocarbon components derived from petroleum sources may be predominately aliphatic or aromatic. Preferred are the aromatic solvents particularly those containing alkylated benzenes and naphthalenes.

- 10 The adjuvants generally contain, in percent by weight relative to the total weight of the adjuvant, from 2 to 30 percent anionic surfactant (a); from 1 to 20 percent fatty acid (b) (i) or from 10 to 96 percent lower alkanol ester (b) (ii); and from 90 to 10 percent hydrocarbon component (c). More preferably, the adjuvant  
15 contains from 2 to 10 percent anionic surfactant (a); from 4 to 10 percent fatty acid (b) (i) or from 10 to 50 percent lower alkanol ester (b) (ii); and from 88 to 40 percent hydrocarbon component (c). The hydrocarbon component is optional when the (b) component is a fatty acid ester.

20

One preferred series of adjuvants is available from BASF Corporation, Mt. Olive, NJ, USA under the DASH® family of adjuvants, which contain:

- 25 (a) 20-25% phosphate ester anionic surfactant derived from nonionic polyether having a molecular weight of about 800 Daltons, e.g. Klearfac® AA270;  
(b) 30-40% C<sub>1</sub>-C<sub>6</sub>-alkanol ester of a fatty acid having 4-22 carbon atoms which is approximately a 1:1 blend of methyloleate and  
30 methylpalmitate, e.g. C65® methylester;  
(c) 2-10% oleic acid; and  
(d) 30-40% mixture of alkylated benzenes and naphthalenes e.g. Aromatic® 150 solvent.

- 35 A particular preferred adjuvant product, as described in US 4,834,908, is:

- (a) 22,5% Klearfac® AA270 (phosphate ester anionic surfactant derived from nonionic polyether having a molecular weight of  
40 about 800 Daltons) (available from BASF Corporation, Mt. Olive, NJ, USA);  
(b) 37,5% C65® methylester (lower alkanol ester of a fatty acid having 4-22 carbon atoms which is approximately a 1:1 blend of methyloleate and methylpalmitate derived from natural  
45 sources) (available from Stepan Chemical Co.);  
(c) 5% oleic acid (carboxylic acid);

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- (d) 35% Aromatic<sup>®</sup> 150 solvent (mixed aromatic solvent) (available from Exxon Chemical Corporation).

The final concentration of adjuvant applied will depend upon the specific application (crop, pest, etc.) as well as the activity of the insecticide but it will typically be in the range of 0.5 to 99.5%. Preferably, the amount of adjuvant will be 0.25% to 7% of the spray mix. More preferably, the amount of adjuvant will be 0.25% to 4.0% of the spray mix. Most preferably, the amount of adjuvant will be 0.25 to 1.0% of the spray mix. It is contemplated that the adjuvant can make up as high as 99% of the applied mixture when a highly concentrated insecticidal compound is used, such as in ultra low volume application in which the adjuvant and carrier may be one and the same.

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The adjuvant is typically applied at a rate of from 0.5 l/ha to 2 l/ha, with the preferred rate being about 1 l/ha.

Optional Ingredients Useful in the Practice of the Present Invention:

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Optionally, the insecticidal compositions of the present invention may be blended with a wide variety of other agricultural adjuvants, diluents or carriers, including, but not limited to organic solvents, petroleum distillates, water or other liquid carriers, surface active dispersing agents, finely divided inert solids, etc.

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Also, tank mixes may be made of the insecticidal composition of the present invention with other herbicides, fungicides, plant growth regulators, plant nutrients, and other crop protection and/or crop management chemicals.

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The Utility of the Present Invention:

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The composition of the present invention is useful for controlling economically important pests, including but not limited to: Corn rootworm, wireworm, flea beetle, chafer, cutworm, corn borer, fruit fly, wheat bulb fly, symphylid, mite, alfalfa weevil, aphid, leafhopper, peach twig borer, codling moth, plum curculio, leaf roller, scale, corn earworm, termite, armyworm, bollworm, budworm, boll weevil, looper, lygus, whitefly, thrip, pear psylla, Mexican bean beetle, Colorado potato beetle, greenbug, sorghum shootfly, leafminer, corn rootworm, psyllid, Hessian fly, foliar nematode, billbug, seed corn maggot, seed corn beetle, white grub and other soil insects, mealybug, mosquito, psyllids, cabbageworm, grape moth, spittlebug, and hornworm. The

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composition of the present invention is most preferably used to control pests of the lepidopteran order such as beet armyworm (Spodoptera exigua), tobacco budworm (Heliothis virescens), fall armyworm (S. frugiperda), cabbage looper (Trichoplusia ni), diamondback moth (Plutella xylostella), imported cabbageworm (Pieris rapae) and soybean loopers (Pseudoplusia includens).

The insecticidal composition of the present invention can be applied to crops, including but not limited to bush and vine crops, vegetables, ornamentals, stone fruits, deciduous fruits, forage crops, cereals, citrus, legumes, etc. Exemplary specific crops are mushrooms, avocados, artichokes, asparagus, apples, apricots, almonds, beans, beets, bananas, broccoli, corn, cabbage, caneberries, cranberries, cantaloupes, cauliflower, cherries, coffee, collards, cotton, cucumbers, dewberries, eggplant, grapes, kiwifruit, lettuce, melons, mint, mustard, nectarines, peas, potatoes, peaches, pears, peppers, radishes, squash, strawberries, tea, tomatoes, turf, watermelons, and walnuts. The invention is preferably used to control pests on cotton, okra, green beans, sweet corn, soybeans and potatoes.

Preparation of the Insecticidal Composition of the Present Invention:

The insecticidal composition of the present invention is prepared by blending the adjuvant with the insecticide compound. Exemplary blending techniques are described in the following non-limiting examples: Water is typically used as a diluent in the practice of the present invention. But other diluents can be used as will be apparent to the ordinarily skilled in the art. Other suitable diluents include spray oils such as vegetable, paraffinic or mineral oils. The invention will now be described by referring to the following detailed examples. These examples are set forth by way of illustration and are not intended to be limiting in scope.

#### Example 1: Control of Cotton Aphid

Test plot areas were monitored for the presence of significant naturally occurring populations of the target pest(s). At the critical pest population threshold, treatments were applied to crops using a CO<sub>2</sub> pressurized backpack sprayer. The application methods were designed to simulate commercial ground application of crop protection products that is normally carried out with spray tractors equipped with a spray tank, a pressure pump and a spray rig with nozzles.

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Treatments A-D and F were applied to cotton at the 9th-main stem node growth stage (early-to-mid season) with the sprayer calibrated to deliver 500 l/ha at 275 kPa pressure (through three 12 SX hollow cone nozzles. One plot (E) was left untreated as a control. Each test plot consisted of a 5 m long row of crop and each treatment was replicated four times in a randomized complete block design. Counts on a natural infestation of cotton aphid were made 2 days after the treatments were applied by searching 5 cotton leaves per each treatment plot are presented in Table 1.

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Treatments G-L and N were applied to okra at the 2-3 true leaf growth stage (seedling plants) with the sprayer calibrated to deliver 280 l/ha at 275 kPa) through one 12 SX hollow cone nozzles. One plot (M) was left untreated as a control. Each test plot consisted of a 12 m long row of crop and each treatment was replicated four times in a randomized complete block design. Aphid counts (as above) were made 2 days after treatment by searching 20 okra leaves per each treatment plot (Table 2).

Treatments O-Q were applied to okra at the 1-2-leaf growth stage (seedling plants) using a CO<sub>2</sub> pressurized backpack sprayer calibrated to deliver 340 l/ha at 275 kPa through two 12 SX hollow cone drop nozzles, one nozzle on each side of the plant. One plot (R) was left untreated as a control. Each test plot consisted of a 30-ft long row of crop, and each treatment was replicated four times in a randomized complete block design. Aphid counts (as above) were made 2 and 6 days after treatment by searching 50 plants per each treatment plot. The results of cotton aphid control can be seen in the Table 2.

### 30 A. Methyl parathion at Half Rate per hectare:

Methyl parathion (PennCap-M™) was applied at a rate of 0.56 kg of active ingredient (ai) per hectare (ha). This is half the maximum recommended label rate for aphid control. The insecticide was combined with water at a rate of 500 l of water/ha for delivery in the field. The ratio of the insecticides and the water resulted in an insecticide concentration of 0.11%.

### B. Methyl parathion at Half Rate per hectare Plus Adjuvant:

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A mixture as in A was prepared, except that the adjuvant DASH® was added to the insecticide mix at a rate of 2.35 l ai/ha. With the 500 l of water used to deliver the mix the resultant adjuvant concentration was 0.47%.

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C. Oxydemeton-methyl at Full Rate per hectare:

Oxydemeton-methyl (Metasystox-R™) was used at a rate of 0.28 kg ai/ha (full recommended rate for aphid control). The insecticide  
5 was combined with water at a rate of 500 l of water per hectare for delivery in the field. The ratio of the insecticide and the water resulted in an insecticide concentration of 0.056%.

D. Oxydemeton-methyl at Full Rate per hectare Plus Adjuvant:

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A Mixture as in C was used, except that the adjuvant DASH® was added to the insecticide mix at a rate of 2.35 l ai/ha. That rate of adjuvant mixed with the 500 l of water used to deliver the mix resulted in an adjuvant concentration of 0.47%.

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E. Control:

An untreated plot for comparison of aphid control.

20 F. Adjuvant alone:

The adjuvant DASH® was mixed with the 500 l of water used to deliver the mix resulted in an adjuvant concentration of 0.47%.

25 G. Methyl Parathion at Half Rate per hectare:

Methyl parathion was used at a rate of 0.56 kg ai/ha (half the maximum recommended rate for aphid control). The insecticide was combined with water at a rate of 280 l of water per hectare for  
30 delivery in the field. The ratio of the insecticide and the water resulted in an insecticide concentration of 0.20%.

H. Methyl Parathion at Half Rate per hectare Plus Adjuvant:

35 A mixture as in G was used except that the adjuvant DASH® was added to the insecticide mix at a rate of 2.35 l ai/ha. That rate of adjuvant mixed with the 280 l of water used to deliver the mix resulted in an adjuvant concentration of 0.83%.

40 I. Dimethoate at Full Rate per hectare:

Dimethoate (Dimate™) was used at a rate of 0.28 kg ai/ha) (full recommended rate for aphid control). The insecticide mixture was combined with water at a rate of 280 l of water per hectare for  
45 delivery in the field. The ratio of the insecticides and the water resulted in an insecticide concentration of 0.10%.



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J. Dimethoate at Full Rate per hectare Plus Adjuvant:

A mixture as in I was used except that the adjuvant DASH® was added to the insecticide mix at a rate of 2.35 l of active ingredient per hectare. That rate of adjuvant mixed with the 280 l of water used to deliver the mix resulted in an adjuvant concentration of 0.83%.

K. Insecticidal Combination at Full Combined Rate per hectare:

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A mixture of chlorpyrifos (Lorsban™) and dimethoate was used at a rate of 0.19 and 0.16 kg ai/ha, respectively, for a total of 0.35 kg ai/ha (represents about half the recommended rate for aphid control of each active ingredient, but a full rate for the combined active ingredients). The insecticide mixture was combined with water at a rate of 280 l of water/ha for delivery in the field. The ratio of the insecticides and the water resulted in an insecticide concentration of 0.125%.

20 L. Insecticidal Combination at Full Combined Rate per hectare Plus Adjuvant:

A mixture as in K was used except that the adjuvant DASH® was added to the insecticide mix at a rate of 2.35 l ai/ha. That rate of adjuvant mixed with the 280 l of water used to deliver the mix resulted in an adjuvant concentration of 0.83%.

M. Control:

30 An untreated plot for comparison of aphid control.

N. Adjuvant alone:

The adjuvant DASH® was mixed with the 280 l of water used to deliver the mix resulted in an adjuvant concentration of 0.83%.

O. Mixture of Chlorpyrifos and Dimethoate at Full Rate:

A mixture of chlorpyrifos and dimethoate was used at a rate of 0.415 and 0.337 kg ai/ha, respectively, for a total of 0.75 kg ai/ha. The insecticide mixture was combined with water at a rate of 340 l of water/ha for delivery in the field. The ratio of the insecticides and the water resulted in an insecticide concentration of 0.223%.

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P. Mixture O Plus Adjuvant:

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A mixture as in O was used except that the adjuvant DASH® was added to the insecticide mix at a rate of 2.35 l ai/ha. That rate of adjuvant mixed with the 340 l of water used to deliver the mix resulted in an adjuvant concentration of 0.69%.

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Q. Mixture at Reduced Rate per hectare Plus Adjuvant:

A mixture as in O was used except that DASH® adjuvant was added at 0.69% (as in B) to the insecticide mix, and the insecticide  
10 rates were lowered to 0.2 kg ai/ha of chlorpyrifos and 0.17 kg ai/ha of dimethoate for a total of 0.37 kg ai/ha and final insecticide concentration of 0.11%.

R. Control:

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An untreated plot for comparison of aphid control.

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Table 1: Cotton aphid control in cotton

Treatment	Rate of active ingredient (kg/ha)	Water volume used to deliver (l/ha)	Concentration of the insecticide mix	Concentration of Adjuvant in the tank-mix	Cotton aphid count 2 days after treatment (% control)
E. Untreated control	---	---	---		1277
A. Methyl parathion	0.56	500	0.11%		293 (77)
B. Methyl parathion + Dash®	0.56 2.25	500	0.11%	0.47%	86 (93)
C. Oxydemeton-methyl	0.28	500	0.056%		74 (94)
D. Oxydemeton-methyl + Dash®	0.28 2.25	500	0.056%	0.47%	38 (97)
F. Dash®	2.25	500		0.47%	905 (29)

\* percent control appears in parenthesis

Table 2: Cotton aphid control in Okra

Treatment	Rate of active ingredient (kg/ha)	Water volume used to deliver the insecticide mix (l/ha)	Concentration of the insecticide mix	Concentration of Adjuvant in the tankmix	Cotton aphid count 2 days after treatment (% control)*	Cotton aphid count 6 days after treatment (% control)*
M. Untreated control	---	---	---		132	
G. Methyl parathion	0.56	280	0.2%	-	21 (84)	
H. Methyl parathion+ Dash	0.56 2.25	280	0.2%	0.83%	8 (94)	
I. Dimethoate	0.28	280	0.10%		19 (86)	
J. Dimethoate + Dash	0.28 2.25	280	0.10%	0.83%	11 (92)	
K. Chlorpyrifos+ Dimethoate	0.19 0.16 0.35	280	0.125%		9 (93)	
L. Chlorpyrifos+ Dimethoate + Dash	0.19 0.16 0.35 2.25	280	0.125%		4 (97)	
N. Dash	2.25	280		0.83%	98 (26)	
R. Untreated control	---	---	---	0.83%	229	156
O. Chlorpyrifos + Dimethoate	0.415 0.335 0.75	340	0.223%		69 (70)	14 (91)

Treatment	Rate of active ingredient (kg/ha)	Water volume used to deliver the insecticide mix (l/ha)	Concentration of the insecticide mix	Concentration of Adjuvant in the tankmix	Cotton aphid count 2 days after treatment (% control)*	Cotton aphid count 6 days after treatment (% control)*
P. Chlorpyrifos + Dimethoate + Dash	0.415 <u>0.335</u> 0.75 2.25	340	0.223%		32 (86)	26 (83)
Q. Chlorpyrifos + Dimethoate + Dash	0.2 <u>0.17</u> 0.37 2.25	340	0.11%	0.69%	77 (66)	47 (70)

\* percent control appears in parenthesis

As demonstrated by the above data, cotton aphid control by methyl parathion and a tank mix of chlorpyrifos and dimethoate at rates below the recommended maximum rate for aphid control was much  
5 higher when tank-mixed with the adjuvant than when applied alone, at the application rates tested. Improvement in aphid control was observed by tank-mixing oxydemeton-methyl, dimethoate and blends of dimethoate with chlorpyrifos at the full rate with the adjuvant. These results indicate that the use of the adjuvant in  
10 combination with certain organophosphate insecticides increases the efficacy of control of these insecticides against cotton aphid, even at less than the maximum recommended application rate, as compared to the same insecticides alone.

#### 15 Example 2 - Control of Whiteflies

Test plot areas were monitored for the presence of significant naturally occurring populations of the target pest(s). At the critical pest population threshold, treatments were applied to  
20 crops using a CO<sub>2</sub> pressurized backpack sprayer. The application methods were designed to simulate commercial ground application of crop protection products that is normally carried out with spray tractors equipped with a spray tank, a pressure pump and a spray rig with nozzles.

25 Treatments A - D were applied to green beans at the fruiting growth stage with the sprayer calibrated to deliver 700 l/ha at 275 kPa pressure through 12 SX hollow cone nozzles. One plot (E) was left untreated as a control. Each test plot consisted of a  
30 10-ft long row of crop and each treatment was replicated four times in a randomized complete block design. A natural infestation of whitefly adults was counted 1 and 3 days after treatment by searching 10 leaves per each treatment plot. To determine control over immatures, 3 plants were shaken so that adults flew  
35 away. The shaken plants were then covered with a bag. At 7 days after treatment, the plants were cut down and frozen. The adults inside the bags were brushed onto a petri dish and counted. The whitefly counts are presented in Table 3.

40 Treatments F - I were applied to green beans at the 3-4<sup>th</sup> leaf growth stage with the sprayer calibrated to deliver 340 l/ha at 275 kPa pressure through 12 SX hollow cone nozzles. One plot (J) was left untreated as a control. Each test plot consisted of a  
45 6 m long row of crop and each treatment was replicated four times in a randomized complete block design. Whitefly counts were made

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1, 3 and 7 days after treatment by searching 18 leaves per each treatment plot. The whitefly counts are presented in Table 3.

Treatments K - M were applied to green beans at the 3-4<sup>th</sup> leaf growth stage with the sprayer calibrated to deliver 340 l/ha at 275 kPa pressure through 12 SX hollow cone nozzles. One plot (N) was left untreated as a control. Each test plot consisted of a 6 m long row of crop and each treatment was replicated four times in a randomized complete block design. Whitefly counts were made 1 and 3 days after treatment by searching 18 leaves per each treatment plot. The trial was terminated after the third day due to cold and rainy weather. The whitefly counts are presented in Table 3.

## 15 A. Control:

An untreated plot for comparison of aphid control.

## B. Chlorpyrifos and dimethoate:

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A mixture of chlorpyrifos and dimethoate were used at a rate of 0.56 and 0.425 kg ai/ha, respectively, for a total of 1.0 kg ia/ha. The tankmix rate of 1.0 kg ai/ha represents the minimum labeled rate for whitefly control for each active ingredients.

25 The insecticide mixture was combined with water at a rate of 340 l of water/ha for delivery in the field. The ratio of the insecticides and the water resulted in an insecticide concentration of 0.29%.

## 30 C. Chlorpyrifos and Dimethoate Plus Adjuvant:

A mixture as in G was prepared, except that the adjuvant DASH® was added to the insecticide mix at a rate of 2.35 l ai/ha. With the 340 l of water used to deliver the mix the resultant adjuvant concentration was 0.69%.

## D. Acephate:

40 Acephate (Orthene® 90 S) was applied at a rate of 0.56 of active ingredient (ai) per hectare (ha). The 0.56 kg ai rate represents the minimum labeled rate of acephate for whitefly control. The insecticide was combined with water at a rate of 340 l of water/ha for delivery in the field. The ratio of the insecticides and the water resulted in an insecticide concentration of 0.16%.

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## E. Acephate Plus Adjuvant:

A mixture as in I was prepared, except that the adjuvant DASH® was added to the insecticide mix at a rate of 2.35 l ai/ha. With 5 the 340 l of water used to deliver the mix the resultant adjuvant concentration was 0.69%.

## F. Control:

10 An untreated plot for comparison.

## G. Chlorpyrifos and Dimethoate at Half rate per hectare:

A mixture of chlorpyrifos and dimethoate were used at a rate of 15 0.28 and 0.225 kg ai/ha, respectively, for a total of 0.5 kg ai/ha. The tankmix rate of 0.5 kg ai represents half of the minimum labeled rate for whitefly control for each active ingredients. The insecticide mixture was combined with water at a rate of 340 l of water/ha for delivery in the field. The ratio of the 20 insecticides and the water resulted in an insecticide concentration of 0.15%.

## H. Chlorpyrifos and Dimethoate Plus Adjuvant:

25 A mixture as in G was prepared, except that the adjuvant DASH® was added to the insecticide mix at a rate of 2.35 l ai/ha. With the 340 l of water used to deliver the mix the resultant adjuvant concentration was 0.69%.

## 30 I. Acephate:

Acephate (Orthene® 90 S) was applied at a rate of 1.12 kg of active ingredient (ai) per hectare (ha). The 1.12 kg ai rate of acephate represents the full (maximum) recommended rate for whitefly control. The insecticide was combined with water at a rate 35 of 340 l of water/ha for delivery in the field. The ratio of the insecticides and the water resulted in an insecticide concentration of 0.33%.

40 J. Control:

An untreated plot for comparison.

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Table 3 - Control of Bandedwinged Whitefly in Green Beans

Treatment	Rate of active ingredient (kg/ha)	Water volume used to deliver the insecticide mix (l/ha)	Concentration of the insecticide in the tankmix	Concentration of adjuvant in the tankmix	# Whitefly adults counted (% control)			
					Days After Treatment:			
					1	3	7	
A. Untreated check	---				637	1077	2821	
B. Untreated check	---				610	582	527	
C. chlorpyrifos + Dimethoate	1.0	340	0.29%		174 (71)	61 (89)	1137 (0)	
D. chlorpyrifos + Dimethoate + Dash®	1.0 + 2.25	340	0.29%	0.69%	36 (94)	62 (89)	250 (53)	
E. Acephate	0.56	340	0.16%		24 (96)	10 (98)	54 (90)	
F. Acephate + Dash®	0.56 + 2.25	340	0.16%	0.69%	18 (97)	10 (98)	99 (81)	
N. Check	---				472	462		
K. chlorpyrifos + Dimethoate	0.5	340	0.15%		69 (85)	52 (89)		
L. chlorpyrifos + Dimethoate + Dash®	0.5 + 2.25	340	0.15%	0.69%	25 (95)	32 (93)		
M. Acephate	1.12	340	0.30%		11 (98)	8 (98)		

These data show that the addition of the adjuvant to tankmixes of chlorpyrifos +dimethoate at the minimum labeled rate or half the minimum labeled rate for whitefly control resulted in better

5 knockdown and residual control of bandedwinged whitefly as compared to the insecticide tankmix at the same rates alone. Furthermore, the above insecticides plus Dash had comparable control to acephate at the full rate, but were weaker than acephate when

10 result in a reduction of the rates needed for effective whitefly control by the organophosphate insecticides chlorpyrifos and dimethoate.

#### Example 3 - Control of Lepidopterous Pests

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Test plot areas were monitored for the presence of significant naturally occurring populations of the target pest(s). At the critical pest population threshold, treatments were applied to crops using a CO<sub>2</sub> pressurized backpack sprayer. The application

20 methods were designed to simulate commercial ground application of crop protection products that is normally carried out with spray tractors equipped with a spray tank, a pressure pump and a spray rig with nozzles.

25 Treatments A - D were applied to cotton at the fruiting growth stage with the sprayer calibrated to deliver 188 l per hectare at 275 kPa pressure through 12 SX hollow cone nozzles. One plot (E) was left untreated as a control. Each test plot consisted of a 9 m long row of crop and each treatment was replicated four times

30 in a randomized complete block design. Beet armyworm population was counted on a 4 m row section of the plot by using a drop cloth. To assess control of tobacco budworm, the number of damaged bolls in 50 bolls from a 10 square meter plot were counted. The counts were made 3 days after the treatment. The average

35 counts are presented in Table 4.

Treatments F - J were applied to sweet corn at the 1-2 leaf growth stage with the sprayer calibrated to deliver 309 l per hectare at 275 kPa pressure through 12 SX hollow cone nozzles.

40 One plot (K) was left untreated as a control. Each test plot consisted of a 6 m long row of crop and each treatment was replicated four times in a randomized complete block design. Beet armyworm and fall armyworm populations were counted on a 4 m row section of the plot 4 days after treatment. The average counts

45 are presented in Table 5.

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Treatments L and M were applied to soybeans at the fruiting growth stage with the sprayer calibrated to deliver 188 l per hectare at 275 kPA pressure through 12 SX hollow cone nozzles. One plot (N) was left untreated as a control. Each test plot consisted of 0.6-3 m long rows of crop and each treatment was replicated four times in a randomized complete block design. Soybean looper populations were counted on a 4 meter square section of each plot 3 days after treatment. The trial was terminated thereafter due to cold rainy weather. The average counts are presented in Table 6.

## A. Chlorpyrifos and dimethoate:

A mixture of chlorpyrifos and dimethoate were used at a rate of 0.415 and 0.28 kg ai/ha, respectively, for a total of 0.7 kg ai/ha. The rate of chlorpyrifos used is half the minimum recommended rate for beet armyworm control, whereas dimethoate is not labeled for beet armyworm control. The insecticide mixture was combined with water at a rate of 188 l of water/ha for delivery in the field. The ratio of the insecticides and the water resulted in an insecticide concentration of 0.37%.

## B. Chlorpyrifos and Dimethoate Plus Adjuvant:

A mixture as in A was prepared, except that the adjuvant DASH® was added to the insecticide mix at a rate of 2.35 l ai/ha. With the 188 l of water used to deliver the mix the resultant adjuvant concentration was 1.25%.

## C. Chlorpyrifos:

Chlorpyrifos was applied at a rate of 0.56 kg of active ingredient (ai) per hectare (ha). This rate of chlorpyrifos is two-thirds the lowest recommended rate for beet armyworm control. The insecticide was combined with water at a rate of 188 l of water/ha for delivery in the field. The ratio of the insecticides and the water resulted in an insecticide concentration of 0.30%.

## D. Chlorpyrifos Plus Adjuvant:

A mixture as in C was prepared, except that the adjuvant DASH® was added to the insecticide mix at a rate of 2.35 l ai/ha. With the 188 l of water used to deliver the mix the resultant adjuvant concentration was 1.25%.

## E. Control:

An untreated plot for comparison.

## 5 F. Chlorpyrifos and Dimethoate:

A mixture of chlorpyrifos and dimethoate were used at a rate of 0.28 and 0.225 kg ai/ha, respectively, for a total of 0.5 kg ai/ha. The rate of chlorpyrifos used is one-third the minimum recommended rate for beet armyworm control, and half the minimum recommended rate for fall armyworm control, whereas dimethoate is not labeled for beet armyworm or fall armyworm control. The insecticide mixture was combined with water at a rate of 309 l of water/ha for delivery in the field. The ratio of the insecticides and the water resulted in an insecticide concentration of 0.16%.

## G. Chlorpyrifos and Dimethoate Plus Adjuvant:

A mixture as in F was prepared, except that the adjuvant DASH® was added to the insecticide mix at a rate of 2.35 l ai/ha. With the 309 l of water used to deliver the mix the resultant adjuvant concentration was 0.76%.

## H. Chlorpyrifos:

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Chlorpyrifos was applied at a rate of 1.06 kg of active ingredient (ai) per hectare (ha). This rate of chlorpyrifos is the maximum recommended rate for beet and fall armyworm control. The insecticide was combined with water at a rate of 309 l of water/ha for delivery in the field. The ratio of the insecticides and the water resulted in an insecticide concentration of 0.34%.

## I. Chlorpyrifos Plus Adjuvant:

35 A mixture as in H was prepared, except that the adjuvant DASH® was added to the insecticide mix at a rate of 2.35 l ai/ha. With the 309 l of water used to deliver the mix the resultant adjuvant concentration was 0.76%.

## 40 J. Adjuvant alone:

The adjuvant DASH® was mixed with the 309 l of water used to deliver the mix resulted in an adjuvant concentration of 0.76%.

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K. Control:

An untreated plot for comparison.

5 L. Chlorpyrifos and Dimethoate:

A mixture of chlorpyrifos and dimethoate were used at a rate of 0.28 and 0.225 kg ai/ha, respectively, for a total of 0.5 kg ai/ha. The insecticide mixture was combined with water at a rate of 188 l of water/ha for delivery in the field. The ratio of the insecticides and the water resulted in an insecticide concentration of 0.27%.

M. Chlorpyrifos and Dimethoate Plus Adjuvant:

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A mixture as in L was prepared, except that the adjuvant DASH® was added to the insecticide mix at a rate of 2.35 l ai/ha. With the 188 l of water used to deliver the mix the resultant adjuvant concentration was 1.25%.

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N. Control:

An untreated plot for comparison of lepidopteran count.

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TABLE 4 - Control of Beet Armyworm in Cotton and Tobacco Budworm in Cotton

Treatment	Rate of active ingredient (kg/ha)	Water volume used to deliver (l/ha)	Concentration of the insecticide in the tankmix	Concentration of Adjuvant in the tankmix	# Beet Armyworms (% control) 3 days after treatment	% Bolls Damaged by Tobacco Budworm 3 DAT
E. Control	---				112	45
A. Chlorpyrifos + Dimethoate	0.7	188	0.37%		92 (18)	45
B. Chlorpyrifos + Dimethoate + Dash®	0.7+ 2.25	188	0.37%	1.25%	21 (81)	47
C. Chlorpyrifos	0.56	188	0.30%		73 (38)	42
D. Chlorpyrifos + Dash®	0.56+ 2.25	188	0.30%	1.25%	42 (76)	44

TABLE 5 - Control of Beet Armyworm and Fall Armyworm in Sweet Corn

Insecticide	Rate of active ingredient (kg/ha)	Water volume used to deliver (l/ha)	Concentration of the insecticide mix	Concentration of Adjuvant in the tankmix	# Beet Armyworm (% control) 4 DAT	# Fall Armyworm (% control) 4 DAT
K. Control	---				3	5
F. Chlorpyrifos + Dimethoate	0.5	309	0.16%		3 (0)	0.50 (90)
G. Chlorpyrifos + Dimethoate + Dash®	0.5 + 2.25	309	0.16%	0.76%	2 (33)	0 (100)
H. Chlorpyrifos	1.06	309	0.34%		1 (66)	0.25 (95)
I. Chlorpyrifos + Dash®	1.06 + 2.25	309	0.34%	0.76%	1 (66)	0.25 (95)
J. Dash®	2.25	309		0.76%	6 (0)	2 (60)

These results show that chlorpyrifos at half-to-two-thirds the labeled rate for beet armyworm control provided effective and better beet armyworm control when tankmixed with Dash than when 5 applied alone at the same rates. A similar trend was observed on the more susceptible fall armyworm.

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TABLE 6 - Control of Soybean Looper in Soybeans

Treatment	Rate of active ingredient (kg/ha)	Water volume used to deliver (l/ha)	Concentration of insecticide in the tankmix	Concentration of Adjuvant in the tankmix	# Soybean Loopers 3 DAT
N. Control	---				$10 \pm 2$
L. Chlorpyrifos + Dimethoate	0.5	188	0.27%		$12 \pm 5$
M. Chlorpyrifos + Dimethoate + Dash®	0.5 + 2.25	188	0.27%	1.25%	$11 \pm 2$

## Example 4: Control of Thrips in Cotton

Treatments were applied to crops using a CO<sub>2</sub> pressurized backpack  
5 sprayer. The application methods were designed to simulate commercial ground application of crop protection products that is normally carried out with spray tractors equipped with a spray tank, a pressure pump and a spray rig with nozzles.

- 10 Treatments A-F were applied to cotton at the 2-3<sup>rd</sup> true leaf growth stage (seedling plants) with the sprayer calibrated to deliver 138 l per hectare at 275 kPA pressure through two 12 SX hollow cone nozzles. One plot (A) was left untreated as a control. Each test plot consisted of a 20 m long row of crop and  
15 each treatment was replicated four times in a randomized complete block design. Thrips were counted 1-9 days after treatment by collecting 10 cotton plants from each test plot at random, the plants were washed with a water and detergent + bleach solution in the laboratory. The water was then poured onto a coffee filter  
20 and from there thrips were rinsed onto a filter paper to be counted under a scope. The data are presented in Table 7.

A. Untreated control.

- 25 An untreated plot for comparison of control.

B. Acephate at Full Rate per hectare:

- Acephate (Orthene<sup>TM</sup>) was applied at a rate of 0.225 kg of active  
30 ingredient (ai) per hectare (ha). This is the maximum recommended label rate for thrips control. The insecticide was combined with water at a rate of 138 l of water/ha for delivery in the field. The ratio of the insecticides and the water resulted in an insecticide concentration of 0.16%.

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C. Acephate at Full Rate per Acre Plus Adjuvant:

- A mixture as in B was prepared, except that the adjuvant DASH®  
was added to the insecticide mix at a rate of 2.35 l ai/ha. With  
40 the 138 l of water used to deliver the mix the resultant adjuvant concentration was 1.67%.

D. Dicrotophos at Full Rate per hectare:

- 45 Dicrotophos (Bidrin<sup>TM</sup>) was used at a rate of 0.225 kg ai/ha (full recommended rate for thrips control). The insecticide was combined with water at a rate of 138 l of water per hectare for delivery.

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very in the field. The ratio of the insecticide and the water resulted in an insecticide concentration of 0.16%.

E. Dicrotophos at Full Rate per hectare Plus Adjuvant:

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A Mixture as in D was used, except that the adjuvant DASH® was added to the insecticide mix at a rate of 2.35 l ai/ha. That rate of adjuvant mixed with the 138 l of water used to deliver the mix resulted in an adjuvant concentration of 1.67%.

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E. Adjuvant alone:

The adjuvant DASH® was mixed with the 138 l of water used to deliver the mix resulted in an adjuvant concentration of 1.67%.

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TABLE 7 - Control of Thrips in Cotton

Insecticide	Rate of active ingredient (kg/ha)	Water volume used to deliver (l/ha)	Concentration of the insecticide mix (%)	Concentration of Adjuvant in the tankmix (%)	#Thrips/10 Plants <sup>1</sup> (% control) 0 DAT	1 DAT	5 DAT	9 DAT
A. Control	---				252 ± 88	115 ± 50	65 ± 43	36 ± 32
B. Acephate	0.225	138	0.16%		174 ± 50	21 ± 9 (80)	42 ± 17 (35)	20 ± 18 (44)
C. Acephate + Dash	0.225 2.25	138	0.16%	1.67%	164 ± 63	18 ± 13 (84)	36 ± 20 (45)	26 ± 19 (28)
D. Diclotophos (Bidrin 8 EC)	0.225	138	0.16%		228 ± 108	31 ± 12 (73)	36 ± 28 (45)	35 ± 16 (03)
E. Diclotophos + Dash	0.225 2.25	138	0.16%	1.67%	237 ± 123	43 ± 38 (63)	40 ± 11 (38)	27 ± 22 (25)
F. Dash	2.25	138		1.67%	186 ± 31	68 ± 49 (41)	66 ± 25 (00)	52 ± 33 (00)

### Example 5 - Control of Colorado Potato Beetle

The efficacy of Guthion™ (azinphosmethyl) alone and in combination with Dash HC® against the Colorado Potato Beetle (*Leptotarsa decemlineata*) on potatoes.

The test plot area was monitored for the presence of significant naturally occurring populations of the target pest, Colorado potato beetle (CPB). At the critical pest population threshold, treatments were applied to 6 meter, single row plots of the crop using a CO<sub>2</sub> pressurized backpack sprayer.

Treatments were sprayed on potatoes in the early bloom stage to a mature population of the Colorado potato beetle. Larvae were evaluated in two classes: class one = first and second instar larvae, class two = third and fourth instar. Population counts were taken at 3 and 7 days after treatment. Trial results can be seen in Table 8.

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#### A. Untreated Control

An untreated plot for comparison of beetle control.

#### 25 B. Azinphosmethyl at full rate per acre

Azinphosmethyl was applied at a rate of 0.42 kg ai/ha. The recommended rate for CPB control. The insecticide was combined with water at a rate of 600 l/ha. This resulted in an insecticide concentration of 0.07%.

#### C. Azinphosmethyl at 20% reduced rate

Azinphosmethyl was applied at a rate of 0.335 kg ai/ha. This is a 20% reduction below the recommended rate for CPB control. The insecticide was combined with water at a rate of 600 l/ha. This resulted in an insecticide concentration of 0.056%.

#### 40 D. Azinphosmethyl at ½ full rate

Azinphosmethyl was applied at a rate of 0.21 kg ai/ha. This is ½ of the recommended label rate for CPB control. The insecticide was combined with water at a rate of 600 l/ha. This resulted in an insecticide concentration of 0.035%.

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## E. Azinphosmethyl at full rate plus adjuvant

Azinphosmethyl was applied at a rate of 0.42 kg ai/ha. The recommended rate for CPB control. The insecticide was combined with  
5 water at a rate of 600 l/ha. This resulted in an insecticide concentration of 0.07%. With the 600 l of water used to deliver the mix, the resultant adjuvant concentration was 0.383%.

## F. Azinphosmethyl at 20% reduced rate plus adjuvant

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Azinphosmethyl was applied at a rate of 0.335 kg ai/ha. This is a 20% reduction below the recommended rate for CPB control. The insecticide was combined with water at a rate of 600 l/ha. This resulted in an insecticide concentration of 0.056%. With the  
15 600 l/ha of water used to deliver the mix, the resultant adjuvant concentration was 0.383%.

## G. Azinphosmethyl at ½ full rate plus adjuvant

20 Azinphosmethyl was applied at a rate of 0.21 kg ai/ha. This is ½ of the recommended label rate for CPB control. The insecticide was combined with water at a rate of 600 l/ha. This resulted in an insecticide concentration of 0.035%. With the 600 l of water used to deliver the mix, the resultant adjuvant concentration was  
25 0.383%.

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TABLE 8 - Control of Colorado Potato Beetle in Potatoes

Treatment	Rate of active ingredient kg ai/ha.	Total Number of larvae from a six meter plot					
		3 DAT L2	3 DAT L4	7 DAT L2	7 DAT L4		
A. Control	---	29.7	79.3	3.0	24.3		
B. azinphosmethyl	0.42	0.7	12.3	6.0	5.0		
C. azinphosmethyl	0.335	5.0	7.7	1.0	3.0		
D. azinphosmethyl	0.21	4.0	11.7	1.3	6.0		
E. azinphosmethyl + adjuvant	0.42 + 1.0	5.3	1.7	3.3	9.0		
F. azinphosmethyl + adjuvant	0.335 + 1.0	5.0	8.0	0.3	1.3		
G. azinphosmethyl + adjuvant	0.21 + 1.0	1.7	6.3	1.0	5.0		

As demonstrated by the above data, in 12 possible paired comparisons between insecticide performance with and without the adjuvant, the insecticide/adjuvant combination performed better in 8 comparisons (67% of the time). Equivalent in one comparison (8%), and worse than the insecticide alone in 3 comparisons (25%).

#### Example 6 - Control of Cabbage Pests

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The efficacy of chlorpyrifos plus Dash® adjuvant against the cabbage pests: cabbage looper (*Trichoplusia ni*), diamondback moth (*Plutella xylostella*), and imported cabbageworm (*Pieris rapae*) is assessed in this example.

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The test plot area was monitored for the presence of significant naturally occurring populations of the target pests. At the critical pest population threshold, treatments were applied to 6 meter, single row plots of the crop using a CO<sub>2</sub> pressurized backpack sprayer. The trial was sprayed with a 3-nozzle boom: one tip positioned over the center of the row, two tips on drops on either side of the row. Spray volume was 403 l/ha. The cabbage was just beginning to head at application. Each treatment had 3 replicates. Total larvae of each species were counted from 3 plants per plot, on 4 and 7 DAT. Data were statistically analyzed using the SQRT (X+0.5) transformation. The results are presented in Table 9.

#### A. Untreated Control

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An untreated plot for comparison of control.

#### B. Chlorpyrifos at full rate per acre

35 Chlorpyrifos was applied at a rate of 1.44 kg ai/ha, the recommended label rate. The insecticide was combined with water at 403 l/ha. This resulted in an insecticide concentration of 0.35%.

#### C. Chlorpyrifos at 20% reduced rate (80% of label rate)

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Chlorpyrifos was applied at a rate of 1.12 kg ai/ha, a 20% reduction of the recommended label rate. The insecticide was combined with water at 403 l/ha. This resulted in an insecticide concentration of 0.28%.

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D. Chlorpyrifos at  $\frac{1}{2}$  label rate

Chlorpyrifos was applied at a rate of 0.7 kg ai/ha, a 50% reduction of the recommended label rate. The insecticide was combined with water at 403 l/ha. This resulted in an insecticide concentration of 0.173%.

## E. Chlorpyrifos at full rate plus adjuvant

10 Chlorpyrifos was applied at a rate of 1.4 kg ai/ha, the recommended label rate. The insecticide was combined with water at 403 l/ha. This resulted in an insecticide concentration of 0.35%. With the 403 l of water used to deliver the mix, the resultant adjuvant concentration was 0.26%.

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## F. Chlorpyrifos at 80% label rate plus adjuvant

Chlorpyrifos was applied at a rate of 1.12 kg ai/ha, a 20% reduction of the recommended label rate. The insecticide was combined with water at 403 l/ha. This resulted in an insecticide concentration of 0.28%. With the 403 l of water used to deliver the mix, the resultant adjuvant concentration was 0.26%.

G. Chlorpyrifos at  $\frac{1}{2}$  label rate plus adjuvant

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Chlorpyrifos was applied at a rate of 0.7 kg ai/ha, a 50% reduction of the recommended label rate. The insecticide was combined with water at 403 l/ha. This resulted in an insecticide concentration of 0.173%. With the 403 l of water used to deliver the mix, the resultant adjuvant concentration was 0.26%.

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TABLE 9 - Control of Cabbage Pests in Cabbage

Treatment	Rate (kg. ai/ha)	# of larvae							
		4DAT				7DAT			
		TRIPNI	PLUTMA	PIERRA	TRIPNI	PLUTMA	PIERRA	TRIPNI	PIERRA
A. Control	---	1.7	2.3	4.7	0.3	1.7	2.3	0.3	2.3
B. Chlorpyrifos	1.4	0.7	1.0	0	0.7	1.0	1.3	0.7	1.3
C. Chlorpyrifos	1.12	1.3	0.3	0	2.0	0	1.0	2.0	1.0
D. Chlorpyrifos	0.7	2.7	0.7	0	0.7	0.3	0.3	0.7	0.3
E. Chlorpyrifos + Dash®*	1.42 1.0	2.0	0.7	0.7	1.3	0.3	3.0	1.3	3.0
F. Chlorpyrifos + DASH®*	1.12 1.0	3.0	0.3	0	1.0	0.3	1.0	1.0	1.0
G. Chlorpyrifos+ DASH®*	0.7 1.0	3.0	5.0	4.0	0.7	0.7	2.7	0.7	2.7

## Example 7 - Airblast Application

An air blast sprayer utilizes a fan or pump to create a high speed air stream that transports and deposits pesticide solutions in orchard and vine crops to control sucking pests in tree fruits such as aphids, scale crawlers, lygus bug, pear psylla, peach twig borer and leafhoppers.

- 10 The addition of the adjuvant DASH improves the performance of chlorpyrifos by enhancing coverage on both target pests and foliage. The organophosphate insecticide chlorpyrifos is applied at a rate of 0.3 g ai/l of water/ha. DASH adjuvant is included at the rate of 5 ml per liter. The rate range of chlorpyrifos is
- 15 from 0.3-0.6 g ai/l.

Treatments are applied with conventional air blast spray rigs to control sucking pests. This method is representative of a commercial ground application of crop protection products utilized in

20 tree fruits.

## Example 8 - Aerial Application of Organophosphate Insecticide

- The organophosphate insecticide profenofos (Curacron™) is
- 25 aerially applied at 1.12 kg ai/ha in combination with DASH adjuvant at 2.3 l/ha. The insecticide is combined with water at 11-38 liter. The volume of water/ha is determined by crop growth stage and application equipment. The concentration of active ingredient rate of profenofos when sprayed at the above water volumes would be 1.2-4.0%. The addition of adjuvant improves the performance of profenofos by enhancing coverage on both target pests and foliage. The concentration of the adjuvant Dash when sprayed at the above water volumes would be 2.4-8.0%.

- 35 Treatments are aerially applied to control lepidopterous pests such as armyworms and Helicoverpa spp. This application method is representative of commercial aerial applications of crop protection products utilized in cotton.

## 40 Example 9 - Ultra Low Volume Aerial Application

- Area-wide control of migratory locusts in Northern Africa and the Middle East, as well as control of mosquitoes, which vector malaria, yellow fever, and other tropical diseases, requires widespread ultra low volume (ULV) aerial sprays of less than one gallon per acre. In such applications, the adjuvant is combined
- 45 with malathion, chlorpyrifos, or another insecticide, with no

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additional water, other carriers, or additives. Malathion is used at a rate of 0.56 kg ai/ha and is mixed with DASH adjuvant with no additional water, other carriers or additives. The adjuvant-malathion mix is applied at a volume of 9.4 l/ha, and is delivered in the field using an aerial ULV sprayer. The concentration of malathion and adjuvant is 6% for malathion and 94% for adjuvant.

This type of ULV application is common in the tropics where the area to be treated is extensive, and the ground is rugged. The addition of DASH improves the performance of malathion (and other insecticides) by enhancing coverage on both target pests and the surfaces on which they alight.

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## Claims:

1. An insecticidal composition comprising:
  - 5 from 0.015% to 3.6% of one or more organophosphate insecticidal compounds;
  - from 0.5% to 99.5% of an adjuvant composition comprising, based on the weight of the adjuvant:
    - 10 (a) from 20 to 90 weight percent of a C<sub>1</sub>-C<sub>6</sub>-alkanol ester of a fatty acid containing from 4-22 carbon atoms;
    - (b) from 4 to 40 weight percent of an anionic surfactant selected from the group consisting of partial sulfate and phosphate esters and carboxylates of monohydroxylfunctional polyoxyalkylene ethers;
    - 15 (c) from 2 to 20 weight percent of a long chain carboxylic acid containing from 10 to 20 carbon atoms; and
    - (d) optionally, a hydrocarbon;
  - and diluent.
- 20 2. The insecticidal of claim 1 wherein the adjuvant comprises:
  - (a) from 30 to 80 percent of a C<sub>1</sub>-C<sub>6</sub>-alkanol ester of a fatty acid containing from 10 to 20 carbon atoms;
  - (b) from 4 to 20 percent of an anionic surfactant selected from the group consisting of the partial sulfate and
  - 25 phosphate esters and carboxylates of monohydroxyl-functional polyoxyalkylene ethers having an average molecular weight of from 600 to 1200 Daltons; and
  - (c) from 4 to 6 percent of a long chain carboxylic acid having from 10 to about 20 carbon atoms.
- 30 3. The insecticidal composition of claims 1 or 2 wherein the organophosphate is selected from the group consisting of:
  - acephate; formothion; azamethiphos; azinphos-ethyl; azinphos-methyl; chlorpyrifos; chlorfenvinphos; cyanophos; danifos;
  - 35 fensulfothion; tribufos; O,O-diethyl O-[6-methyl-2(1-methyl-ethyl)-4-pyrimidinyl] phosphorothioate; O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate; dicrotophos; dimethoate; dioxathion; disulfoton; endothion; ethion; fenitrothion; ethoprop; chlorethoxyfos; iprobenfos; isazofos; isofenphos; isoxathion; vamidothion; S-[2-(ethyl-
  - 40 sulfinyl)-1-methylethyl] O,O-dimethyl phosphorothioate; methidathion; methyl parathion; alpha isomer of 2-carbomethoxy-1-methylvinyl dimethyl phosphate; beta isomer of 2-carbomethoxy-1-methylvinyl dimethyl phosphate; morphothion; naled;
  - 45 fenamiphos; fosmethilan; pyridaphenthion; omethoate; parathion; phencapton; phenthoate; phorate; phosalone; phosmet; phosnichlor; phosphamidon; leptophos; phoxim; pirimiphos-

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5 methyl; pirimiphos-ethyl; profenofos; prothidathion; prothoate; piperophos; tolclofos-methyl; ronnel; cadusafos; so-phamide; demeton, demeton I (thiono isomer); demeton II (thiolo isomer); oxydemeton-methyl; cyanthoate; tebupirimfos; terbufos; tetra chlorvinphos; thiometon; prothiofos; diali-  
fos; trichlorfon; and combinations of these.

10 4. The insecticidal composition of claims 1 to 3 wherein the organophosphate is selected from the group consisting of: chlorpyrifos; parathion; dimethoate; azinphosmethyl; acephate; diazinon; dicrothophos; malathion; oxydemeton-methyl; ethyl parathion; methyl parathion; ethion; fonofos; and combinations of these.

15 5. The insecticidal composition of claims 1 to 4 wherein the organophosphate is one selected from the group consisting of: methyl parathion; oxydemeton-methyl; dimethoate; acephate; dicrotophos; and azinphosmethyl; and opitonally a second selected from the groups consisting of:  
20 chlorpyrifos; parathion; ethyl methyl parathion; methyl parathion; dimethoate; azinphosmethyl; acephate; diazinon, malathion, ethion; and fonofos.

25 6. The insecticidal composition of claims 1 or 2 wherein the alkanol ester of a fatty acid is derived from C<sub>1</sub>-C<sub>6</sub>-alkanol and wherein said fatty acid has from 10 to 20 carbon atoms.

30 7. The insecticidal composition of claim 6 wherein the lower alkanol ester of a fatty acid is selected from the group consisting of: methyl laurate; methyl myristate; methyl stearate; methyl linoleate; methyl linolenate; methyl oleate; methyl palmitate; and mixtures thereof.

35 8. A method for controlling insect populations in crops comprising: applying to said crop an effective amount of an insecticidal composition as defined in claims 1 to 7.

40 9. The method of claim 8 wherein said insect population is selected from the lepidopteran order.

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 5 741 502 A (ROBERTS JOHNNIE R) 21 April 1998 (1998-04-21) claims 1,2 column 9, line 59 - line 62 ----	1-9
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A	US 4 834 908 A (HAZEN JAMES L ET AL) 30 May 1989 (1989-05-30) cited in the application -----	

☐ Further documents are listed in the continuation of box C.

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